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⑤④ **Glass composition.**

⑤⑦ A glass composition comprises by weight, 50-60%, SiO₂; 5-13%, K₂O; 5-8%, TiO₂; 10-15%, BaO; 5-10%, ZnO; 3-10%, Na₂O; 1-5%, CaO; and 0.3-0.8%, Sb₂O₃.
The density, refractive index and dispersion value of light of the composition are equal to, or higher than, those of conventional lead-containing crystal glass, although the composition is entirely lead free.

This invention relates to a glass composition which looks like, or can be regarded as, crystal glass, although it does not contain lead (Pb) and is suitable for use in producing tableware or like articles.

Conventionally, lead-containing crystal glass is used popularly as crystal glass in producing tableware or like articles. The glass contains a large amount of lead, and such of its characteristics as that "it is massive"; that "it has a high light refraction index and exhibits a high dispersion value of light"; and that "it melts readily", are provided principally by PbO. While the content of PbO varies widely, it generally ranges from 24 to 26 percent by weight.

However, it has recently been questioned whether lead, which is particularly injurious to the human body, can be dissolved out of lead-containing crystal glass. For example, in California, U.S.A., a complaint was filed asserting that the public organization "has not given a clear warning against exposure to lead" arising from lead crystal glass used to produce tableware, decanters and like articles. According to the FDA (Food and Drug Administration) standards of the U.S.A., the permitted level for the dissolution amount of lead has been revised to a rigorously low value.

Meanwhile, in Japan, the dissolution amount of lead from lead-containing crystal glass is regulated by the "Official Announcement No. 84 of the Ministry of Health and Welfare Based on the Food Hygiene Law", and lead-containing crystal glassware makers manufacture lead-containing crystal glass so that the dissolution amount of lead may not exceed the permitted level even where the content of PbO in the lead-containing crystal glass is within 24 to 26 percent. However, it is forecast that the permitted levels may be progressively more restricted in Japan.

Therefore, in order to suppress dissolution of lead from lead-containing crystal glass, Japanese Patent Laid-Open Application No. Heisei 3-205325 has proposed a technique wherein the surface of a piece of lead-containing crystal glass tableware is covered with a protective film which contains silicon oxide as a principal component. However, since the technique requires secondary working after making the glass, a rise in the production cost cannot be avoided.

Another technique has been proposed and is disclosed in Japanese Patent Laid-Open Application No. Heisei 2-141434 wherein the surface of a crystal glass vessel is covered with a lead-free glass layer. With the technique, however, since two kinds of glass are melted simultaneously and sprayed on the crystal glass vessel to mold the lead-free glass layer, there are the problems that the molding process is inefficient, presswork cannot be employed, and so forth.

A further technique is disclosed in Japanese Patent Laid-Open Application No. Heisei 4-50133, wherein the amount of an alkali metal or metals to be added to the total amount of PbO, an alkaline earth metal or metals and ZnO is limited, in order to reduce dissolution of lead. However, the reduction achieved is only about one half.

It is an object of the present invention to provide a novel glass composition which exhibits such characteristics of lead-containing crystal glass as that "it is massive"; that "it has a high refractive index and high dispersion value"; and that "it melts readily" to a degree equal to or higher than that of conventional lead-containing crystal glass, while not containing lead at all.

In order to attain the object described above, according to an aspect of the present invention, there is provided a glass composition, which comprises SiO₂ and K₂O as principal components, 5 to 8 percent by weight of TiO₂ and 10 to 15 percent by weight of BaO.

The content of SiO₂ may be 50 to 60 percent by weight and the content of K₂O may be 5 to 13 percent by weight.

According to another aspect of the present invention, there is provided a glass substrate, which comprises, based on the whole weight of the composition, 50 to 60 percent of SiO₂, 5 to 13 percent of K₂O, 5 to 8 percent of TiO₂, 10 to 15 percent of BaO, 5 to 10 percent of ZnO, 3 to 10 percent of Na₂O, 1 to 5 percent of CaO, and 0.3 to 0.8 percent of Sb₂O₃.

The glass substrate may further comprise, based on the whole weight of the composition, 0 to 1.0 percent of Li₂O, 0 to 2.0 percent of ZrO₂, and 1.0 to 2.0% of B₂O₃.

The contents of the components given above are listed in Table 1 below. It is to be noted that representations of % in the following description are all represented in percent by weight.

Table 1

Component	Content wt%
SiO ₂	50.0 - 60.0
CaO	1.0 - 5.0
BaO	10.0 - 15.0
Na ₂ O	3.0 - 10.0
K ₂ O	5.0 - 13.0
Li ₂ O	0 - 1.0
TiO ₂	5.0 - 8.0
ZnO	5.0 - 10.0
ZrO ₂	0 - 2.0
B ₂ O ₃	1.0 - 2.0
Sb ₂ O ₃	0.3 - 0.8

With the glass composition of the present invention, TiO₂ and BaO are used as raw materials substituted for PbO, and the refractive index and the dispersion value of light are increased by TiO₂, while the density and the refractive index are increased by BaO.

TiO₂ is effective to increase the refractive index and increase the dispersion value (decrease the Abbe number) and is essential as a substitute for PbO in the present invention. Where TiO₂ is less than 5.0%, the target values of the refractive index and the dispersion value cannot be achieved. On the other hand, where TiO₂ exceeds 8.0%, the tendency that the color becomes yellowish increases significantly, and this is undesirable with crystal glass where importance is attached to transparency.

If SiO₂ is less than 50.0%, then the glass composition is inferior in chemical durability, but if SiO₂ exceeds 60.0%, then it is necessary to raise the melting temperature of the glass composition and the density of the glass composition is decreased. While both of BaO and CaO can be employed as an alkaline earth metal, preferably BaO is used in order to assure a high density and a high refractive index. Where BaO is less than 10.0%, the target value of the high density of 2.90 or more cannot be achieved. Where BaO exceeds 15.0%, it is difficult to perform defoaming and the erosion of the furnace material is marked, and accordingly, it is difficult to melt the glass composition. While CaO is effective to lower the viscosity of the glass composition at a high temperature, it is suitably contained by 1.0 to 5.0% in order to assure a high solidifying rate in an operating temperature region.

Alkali components, that is, K₂O, Na₂O and Li₂O are used to lower the melting temperature. Particularly, K₂O is effective and important to suppress development of the color of Fe ions which are an impurity in the glass. The effect is low where K₂O is less than 5.0%, but where it exceeds 13.0%, the erosion of the refractory material is remarkable. Na₂O must necessarily be contained in an amount of at least 3.0% in order to make up for the effect of lowering the melting temperature. Where the total amount of K₂O and Na₂O exceeds 18.0%, the chemical durability of the glass is degraded, and accordingly, it must necessarily be restricted to 18.0% or less. Li₂O has a marked effect of lowering the melting temperature by addition of a small amount, and it is sufficient if it is contained in an amount of 1.0% or less.

ZnO is effective to increase the chemical durability without increasing the hardness of the glass, moderate the viscosity-temperature curve and facilitate the molding operability. The amount of addition is sufficient if within the range of 5.0% to 10.0%.

Since B₂O₃ is effective to lower the melting temperature without increasing the coefficient of thermal expansion by addition of a small amount, it is added in an amount of 1.0 to 2.0%.

Sb₂O₃ has an effect as a defoaming agent in a composition melted at a low temperature, even in such a small amount as 0.3 to 0.8%.

While ZrO₂ is added in order to raise the chemical durability, since it increases the hardness of the glass, it is not preferred with crystal glass, which is in most cases worked by cutting or polishing; and, accordingly, the amount of its addition must be restricted to a minimum.

Due to such actions of the components as described above, a glass composition can be obtained which sufficiently satisfies such requirements for crystal glass that

- (1) the density as representative of massiveness is 2.90 g/cm³ or more;
- (2) the refractive index Nd is 1.55 or more;
- (3) the Abbe number as representative of dispersion is 47 or less;
- (4) the glass composition can be melted readily at a low temperature of 1,370 to 1,380 °C; and
- (5) the coefficient of thermal expansion can be made lower than $100 \times 10^{-7} / ^\circ\text{C}$ taking into consideration that the glass composition is used frequently for tableware.

It is to be noted that it is of course possible to add a coloring agent such as chromium oxide by a small amount to produce colored crystal glass.

As described above, according to the present invention, crystalline glass which has a density, a refractive index and a dispersion value equal to or higher than those of conventional lead-containing crystal glasses can be obtained, although the glass does not contain lead at all. Further, the raw materials are comparatively inexpensive and can be melted at a comparatively low temperature, and accordingly, the glass composition can be produced economically.

When it is considered that the regulations regarding the use of lead are forecast to become progressively more severe, not only from the point of view of dissolution from glassware, but also of the production environment and of the environmental pollution caused by dust and fumes emitted at different stages of production, from the mixing of the raw materials to the blast furnace, the advantage of a glass composition that is entirely free of the highly toxic lead component is very great.

Some non-limiting Examples are now presented to illustrate the invention.

The glass compositions designated Example 1 to Example 7 in Table 2 were mixed, put into respective platinum pots, and melted for about 6 hours at a temperature of 1,375°C in an electric furnace. Thereafter, the pots were taken out, the molten glass materials flowed out onto a steel plate, and then cooled gradually in a lehr. Samples for measurement were then removed, and the density, refractive index, Abbe number and coefficient of thermal expansion of each of the samples were measured. Results of the measurements are listed in Table 2.

It is to be noted that conventional exemplary lead-containing crystal glass has a density of 2.95 to 3.00 g/cm³, a refractive index Nd of 1.555 to 1.565, an Abbe number of 45 to 47 and a coefficient of thermal expansion of $96 \text{ to } 100 \times 10^{-7} / ^\circ\text{C}$.

Table 2

Components & Physical Data	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7
SiO ₂	54.95	54.60	51.15	51.80	50.10	55.50	55.20
CaO	4.00	3.50	5.00	4.00	3.00	1.50	1.50
BaO	12.00	12.50	14.00	13.00	14.50	13.00	13.30
Na ₂ O	3.00	3.50	3.00	5.00	3.00	6.00	9.50
K ₂ O	9.00	10.00	11.00	8.00	12.50	7.00	5.00
Li ₂ O	0.50	0.50	0.50	0.50	0.50		
TiO ₂	7.50	7.00	5.00	8.00	7.00	6.50	5.00
ZnO	7.50	8.00	7.50	8.00	7.00	9.00	9.00
ZrO ₂		1.00	1.00		1.00		
B ₂ O ₃	1.25	1.00	1.50	1.30	1.00	1.00	1.00
Sb ₂ O ₃	0.30	0.40	0.35	0.40	0.40	0.50	0.50
Density(g/cm ³)	2.885	2.908	2.951	2.940	2.955	2.902	2.906
Refraction Index Nd	1.589	1.590	1.588	1.600	1.601	1.582	1.577
Abbe Number	46.5	46.8	48.2	45.5	46.5	47.0	47.0
Coefficient of Thermal Expansion (x 10 ⁻⁷ /°C)	92.6	97.0	101.4	98.3	105.5	94.3	99.5

Claims

1. A lead-free glass composition comprising SiO₂ and K₂O as principal components, 5 to 8% by weight of TiO₂ and 10 to 15% by weight of BaO.
2. A glass composition as claimed in claim 1, wherein the content of SiO₂ is 50 to 60% by weight and the content of K₂O is 5 to 13% by weight.
3. A lead-free glass substrate comprising, based on the total weight of the composition, 50 to 60% of SiO₂, 5 to 13% of K₂O, 5 to 8% of TiO₂, 10 to 15% of BaO, 5 to 10% of ZnO, 3 to 10% of Na₂O, 1 to 5% of CaO, and 0.3 to 0.8% of Sb₂O₃.
4. A glass substrate as claimed in claim 3 and further comprising, based on the total weight of the composition, 0 to 1.0% of Li₂O, 0 to 2.0% of ZrO₂ and 1.0 to 2.0% of B₂O₃.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 93 30 8367

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	EP-A-0 500 325 (NIPPON ELECTRIC GLASS COOMPANY) * claim 1 *	1,2	C03C3/078
X	FR-A-2 091 493 (RADIATION LIM) * claims 1,2 *	1-4	
X	DATABASE WPI Derwent Publications Ltd., London, GB; AN 83-48082K & JP-A-58 060 641 (NIPPON ELECTRIC GLASS) * abstract *	1-3	
P,A	WO-A-92 19559 (VYSOKA SKOLA CHEMICKO-TECHNOLOGICKA USTAVSKLA A KERAMIKY)	1-4	
X	CHEMICAL ABSTRACTS, vol. 117, no. 12, 21 September 1992, Columbus, Ohio, US; abstract no. 117026, YOSHIOKA page 341 ; * abstract * & JP-A-4 092 836 (OHARA KK)	1-4	
A	US-A-3 849 097 (J.W.GIFFEN)		
A	GB-A-2 115 403 (CARL ZEISS STIFTUNG) * claims 1,7,12 *	1-4	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24 January 1994	Examiner LIBBERECHT, E
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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